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Title:

A procedure for optimal calibration for a QCM electronic nose. Relation with specifications for pear quality.

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Summary:

The *"Rome Tor Vergata"* electronic nose has eight Quartz Microbalance Sensors. When a mass is absorbed or placed onto the quartz crystal surface, the oscillation frequency changes in proportion to the amount of mass.

Despite previous studies, no QCM calibration statement has been made in relation to the sensitivity needed in the sensors for pear quality assessment.

A calibration procedure has been designed and precision, sensitivity, specificity and reproducibility, on a QCM based electronic nose, evaluated.

Using data of emission for pear, determinated by GC, it has been evaluated the extracted metrology features in relation to the specifications of the sensing device needed for quality assessment in pears.

A procedure for optimal calibration for a QCM electronic nose. Relation with specifications for pear quality.

(00-PH-041)

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Introduction

Quartz crystal microbalances (QCM) are piezoelectric devices. To turn a quartz crystal into a chemical sensor it is necessary to coat it with a layer of a material capable of capturing molecules from the environment. When a mass is absorbed or placed onto the quartz crystal surface, the oscillation frequency changes in proportion to the amount of mass.(Di Natale et al. 1997)

The ability to control a QCM´s selectivity by applying different coatings is an important feature, and makes this sensor type extremely versatile. However, the coating of QCM is, ironically, their greatest drawback.. Batch-to-batch variability in the manufacturing leads to inadequate reproducibility (Sarig 1998). Indeed, the response of sensors depends on numerous factors that may be difficult to control, such as the temperature and the humidity of the carrier gas. All these factors cause changes in the selectivity of sensors affecting the reproducibility of measurements.

The detection threshold of the human nose is typically between 1000 ppm and <1ppt. Therefore, the absolute detection threshold of a gas sensor should be very low. QCM e-nose, only a few molecules are required to react with the sensitive elements leading to sensitivities close to the ppm or tenth of a ppm range as measured in the vapour phase (Mielle 1996) . Despite previous studies, no QCM calibration statement has been made in relation to the sensitivity needed in the sensors for pear quality assessment.

Objectives

1.To design a calibration procedure and to evaluate metrology features: precision, sensitivity, specificity and reproducibility, on a QCM based electronic nose.

2.To evaluate the extracted metrology features in relation to the specifications of the sensing device needed for quality assessment in pears.

Materials and Methods

The *"Rome Tor Vergata"* electronic nose has eight Quartz Microbalance Sensors coated by different pyrrolic macrocycle solid-state films. The sensors are housed in a test chamber having a volume of about 20ml. Each sensor has a fundamental frequency of 20MHz and it

is part of an oscillator circuit. The measurement of frequency is performed on-board by dedicated electronics. The instrument works connected to a personal computer via a serial link. Dedicated software runs on the PC .The magnitude of the signals is Hz. The users program establishes a reference with a starting point of 0Hz. Namely each measurement is subtracted by the first oscillating frequency value, obtaining an ΔF value (Hz). The variable used as sensor response is the increment between the stabilised values of measured signal with respect the stabilised values of cleaning signal (ΔF_2-ΔF_1).
Two different types of experiments have been carried out:

1. metrology analysis of the QCM e-nose for most relevant chemicals for pear volatiles
2. evaluation of the reproducibility of the electronic nose for a selected reference (propanol) throughout a year of measurements (September 99- May 2000, 400 work hours)

In Experiment 1 following texts were performed:

- determination of the response level of the sensor array using seven chemical compounds (ethyl, propyl and hexyl acetate, propanol, ethanol, butanol and acetaldehyde) relevant for pear volatile emission, with three repetition per session and chemical. Two ml of headspace were injected into the e-nose chamber.
- determination of the sensors´ precision using ethyl acetate and propanol with three repetition per chemical and injecting 2 ml of headspace into sensor chamber.
- determination of the sensitivity of the sensor array to propanol & ethyl acetate by injecting into the sensor chamber 1, 2 and 3 ml of the headspace generated by those chemical, with three repetition per session and chemical.

For both experiments headspace generation was carried out on 50ml hermetic bottles filled to a 10%. Whenever the equilibrium between the gas and liquid phase is achieved, the concentration of the product in the headspace may be derived form the vapour pressure of each chemical. Different volumes extracted from the reference bottles are diluted inside the air chamber of the e-nose for estimating the sensitivity of the e-nose. For Experiment 2 the e-nose worked under dynamic air flow (no dilution of headspace that is higher response of sensors) while for Experiment 1 the headspace was injected into the e-nose chamber (dilution of headspace, that is minor response of sensors).

Results and Discussion

1. Calibration

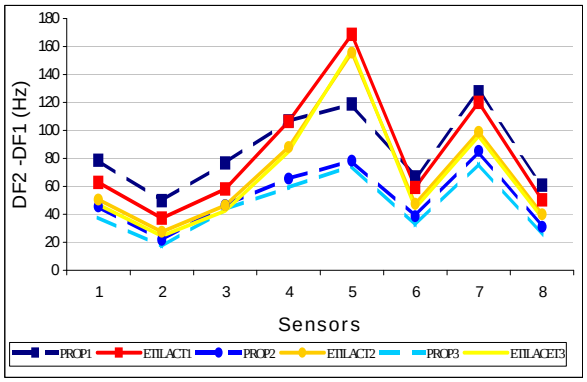
At a preliminary first stage a review of the response level of the QCM sensors with regard to seven chemical compounds, was carried out. Table 1 shows the mean value of the sensor responses (ΔF_2-ΔF_1) for the seven products considered. Sensors response in decreasing order is S5, S7, S4, S3, S1, S6, S8 and S2, the last being sensor with lowest response.

Table 1

	S5	**S7**	**S4**	**S3**	**S1**	**S6**	**S8**	**S2**
Mean (Hz)	120.70	77.85	66.54	49.26	41.15	39.47	31.14	20.77
STD (Hz)	13.93	12.40	10.75	14.35	8.91	8.08	7.94	7.11

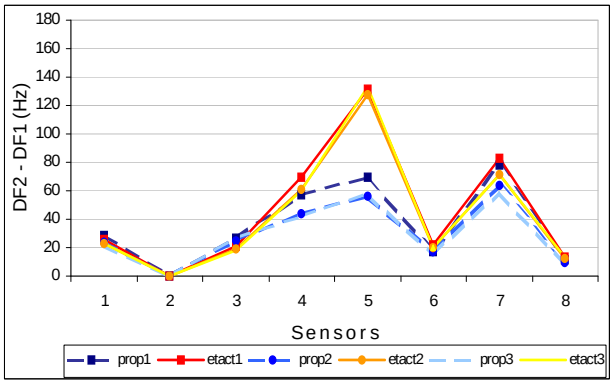
Under a following step, a study on the precision of the sensors´ measurements was performed.

Figure 1. Raw data (no calibration)



CV%	S1	S2	S3	S4	S5	S6	S7	S8
Propanol	39.9	59.9	32.7	33.5	27.1	40.1	28.4	48.7
Etilacet	15.2	22.8	14.5	15.1	7.6	16.8	13.7	17.3

Figure 2. Proposed calibration procedure



S1	S2	S3	S4	S5	S6	S7	S8
16.3	-	4.3	17.3	11.6	6.2	14.6	14.7
6.2	-	5.2	10.5	4.4	6.1	9.9	4.3

Figure 1 shows the time effect on the response of the QCM sensors within a working session of 8 hours duration. A consistent decrease in the (ΔF_2-$\Delta F1$) parameter extracted from the sensors is shown. However, the shape of the "multisensor" spectra remains unchanged. Since sensor 2 showed the lowest response to the chemical compounds of interest, it was used to normalise the "multisensor" spectra. Normalisation consisted of subtracting to each sensor the response of sensor 2. This operation aimed to remove unknown sources of variation other than that of the chemical composition of the headspace for pears. Figure 2 shows the results achieved with this proposed calibration procedure. The CV decrease shows the improvement by the proposed calibration method.

2. Precision

After calibration, precision is computed for each sensor (i:1,3-8) as the standard deviation (STD) of data obtained for replications under similar conditions. Seven STD (n=3) are obtained per sensor corresponding to each of the chemicals evaluated as references. (j=1-7). Precision levels lay around 3.6 hz.

Table 2

STD, p(Hz)	S1	S3	S4	S5	S6	S7	S8
Ethyl acetate	1.514376	1.379613	4.99433	2.715388	1.011599	6.61085	0.4163
Propanol	4.005413	1.135782	8.237313	7.093894	1.021437	9.733961	1.4189

3. Sensibility

This parameter is computed for two different chemical (ethyl acetate, propanol) and for seven sensors (i=1,3-8) by means of the ratio response Δf(Hz) / concentration(mg/l). Maximum sensitivity is found for ethyl acetate in comparison to propanol (figures 3&4), and for sensors 5 and 7 when compared to the rest of sensors.

Figure 3. Ethyl acetate

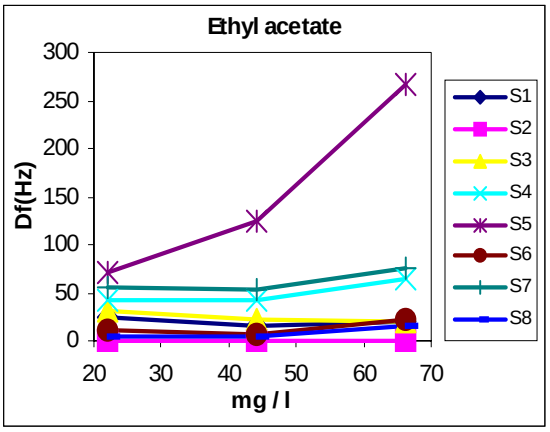


Figure 4. Propanol

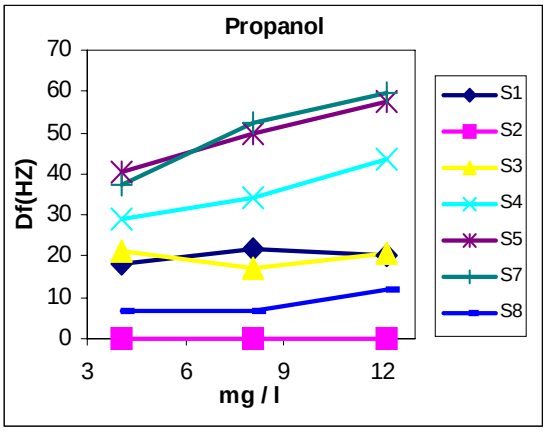


Table 3

Average sensitivity, S (Hz/mg/l)	S1	S3	S4	S5	S6	S7	S8
Ethyl acetate	0.339	0.249	0.571	4.424	0.441	0.588	0.249
Propanol	0.608	0.979	1.767	2.122	0.443	2.739	0.649

4. Specificity

Table 4

Δf_{si}/sum (Δf_{si}, j=1-7)	S1	S3	S4	S5	S6	S7	S8
Ethyl acetate	0.142	0.098	0.198	**0.310**	0.165	0.182	0.120
Propyl acetate	0.175	0.107	0.127	0.096	0.147	0.121	**0.265**
Hexyl acetate	0.135	0.127	0.095	0.048	0.098	0.089	0.158
Propanol	0.140	0.105	0.117	0.072	0.204	0.141	0.150
Butanol	0.117	0.102	0.104	0.071	0.077	0.108	0.132
Ethanol	0.178	0.158	0.154	0.116	0.144	0.176	0.137
Acetaldehyde	0.114	**0.303**	0.205	**0.286**	0.165	0.182	0.038

This metrology feature refers to the degree of selectivity of a sensing device with regard to various stimulus coming from the sample, different from that which is meant to be measured. In our case we compute for each sensor Δf_{si}/sum (Δf_{si}, j=1-7) since those are the

expected chemical to be found in the headspace generated by pears. As expected a low specificity is found for all the sensors. Ethyl acetate and acetaldehyde show higher specificity for sensors 3 and 5 (0.31 and 0.286 respectively) when compared to the rest of sensors. Sensor 8 shows a certain specificity (0.265) for propyl acetate.
The test must be repeated with artificial aromas, made using mixtures of the seven chemicals compounds seen in this test, trying to obtain a concentration of the headspace similar to generated for a pear fruit.
Differences in Specificity for the 8 sensors with regard to chemical, generates variations in the fingerprint or e-nose spectra, which gives good perspectives for qualitative analysis of the headspace. Only those chemicals with high specificity will lead, when are present in the headspace, to significant changes in the fingerprint or e-nose spectra. The rest of volatiles will be indistinguishable but quantitative analysis of overall concentration ca be faces as shown in paragraph 6.

5. Reproducibility

This feature refers to the degree of approximation of different measurements for a magnitude computed either with different methods, measuring devices, measuring conditions (temperature, relative humidity). In our case, the repeatability of the response of the e-nose (average of Δf_{si}) for propanol as a reference has been computed between September 99 until May 2000 for a 400 hours work hours. A cycle of variation is found in the level of response which corresponds to changes in the relative humidity of the ambient. A calibration of changes based on the daily response of the e-nose to propanol (see Figures 5 & 6) enables to improve the reproducibility level from (11.23 Hz) to (3.26 Hz) laying proximate to the precision level.

Figure 5. Propanol-Raw data

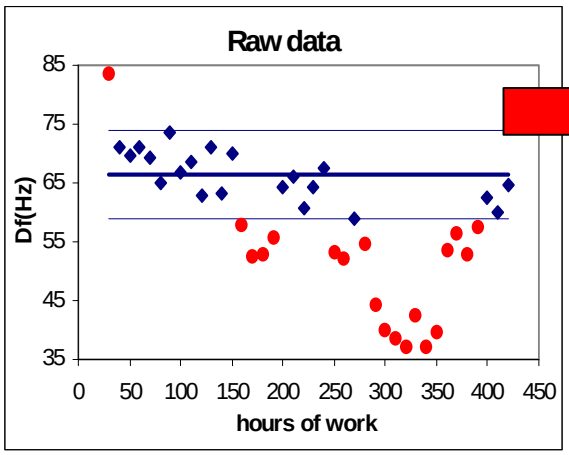
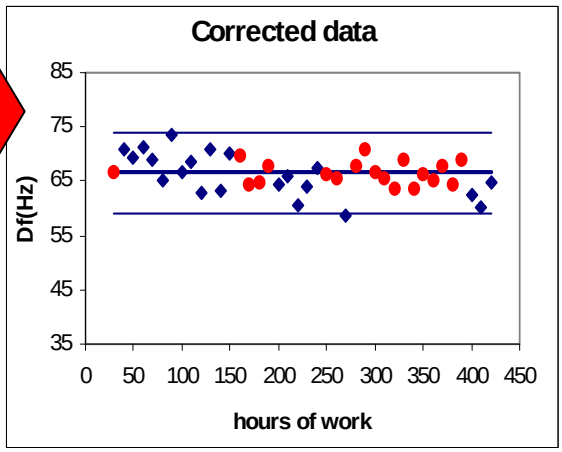


Figure 6. Propanol-Corrected data



	Raw data
Mean (Hz)	58.798
STD (Hz)	11.229

	Corrected data
Mean (Hz)	66.371
STD (Hz)	3.260

It will be necessary to adjust a mathematical model of the sensor signal as a function of the relative humidity and others parameters to obtain a proper correction function.

6. Specifications of an e-nose for volatile evaluation of pears

Lopez et al, 2000 have quantified (ppm/fruit h) a wide number of the volatiles emitted by pears c.v. *Doyenne du Comice* from different maturity stages at harvest, as well as different commercial storage treatments; dynamic headspace generation combined with gas chromatography is used.

Figures 7 summarise the maximum differences between pear batches in volatile emission – *E(ppm/fruit h)* for ethyl acetate and for overall volatiles (ethyl acetate, propyl acetate, butyl acetate, 2-metylbutyl acetate, pentyl acetate, hexyl acetate, ethanol, propanol, 2-metylpropanol, butanol, 2-metylbutanol and hexanol).

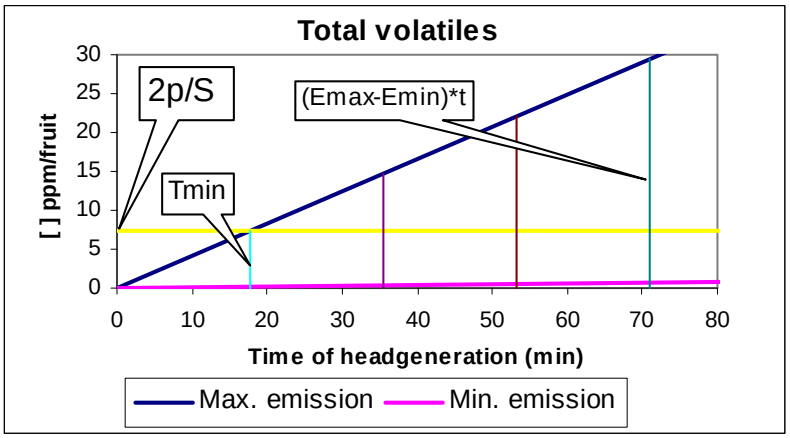
The minimum headspace generation time (*Tmin*) can be derived form considering the minimal concentration needed to reach a sensor response (Hz) equal or higher to the twice precision level -2*p(Hz)*, either a particular or average sensor may be considered-. The amount of classification categories that may be reached between extreme emission levels ($E_{max}(ppm/fruit \cdot h) - E_{min}(ppm/fruit \cdot h)$) can also be computed for increasing duration of the headspace generation based on the expected sensitivity (*S(Hz/ppm)*) either to a specific chemical or to overall volatiles (see Equation 1).

This is a theoretical approach using *S (Hz/ppm)*, it necessary to refer the sensibility previously as Hz/(mg/l) to Hz/ppm, to obtain the real values of minimum time to distinguish between different categories of maturity stage of pear.

Equation 1

$$n = \frac{(Emax(ppm/\ fruit \cdot h) - Emin(ppm/\ fruit \cdot h)) \times t(h) \times S(hz/\ ppm)}{2\,p(hz)}$$

Figure 7



For cualitatives purposes $\frac{2p/S}{(Emax-Emin)\times t}$ should be below **0.1** (Barreiro et al, 2000).

Conclusions

A calibration procedure is proposed using sensor 2 to normalise the response level for the remaining sensor (i=1, 3-8).

Chemometrics parameters of QCM e-nose have been calculated:

- Precision wich lay around 3.6 hz.
- Sensitivity. Maximum sensitivity is found for sensors 5, 7 and 4, which show at the same time the lowest precision.
- Specificity. Sensors 3 and 5 show higher specificity for ethyl acetate and acetaldehyde. Sensor 8 shows a certain specificity for propyl acetate. These chemical compound could be used in the Tor Vergata e-nose for qualitative analysis due to a higher specificity of this nose to this compounds when compared to the rest of chemical
- Reproducibility. A cycle of variation is found in the level of response which corresponds to changes in the relative humidity of the ambient. A calibration method is proposed to improve the reproducibility level.

Knowing the maximum and minimum emission in ppm/(fruit x hour), it may be stablished the specifications of an e-nose for volatile evaluation of pears and then it could be calculated the minimum time of headspace generation to can distinguished between 1, 2, 3 and 4 volatile quality stage of pear fruit, based on worky of e-nose sensors defined for the metrology parameters above calculated.

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